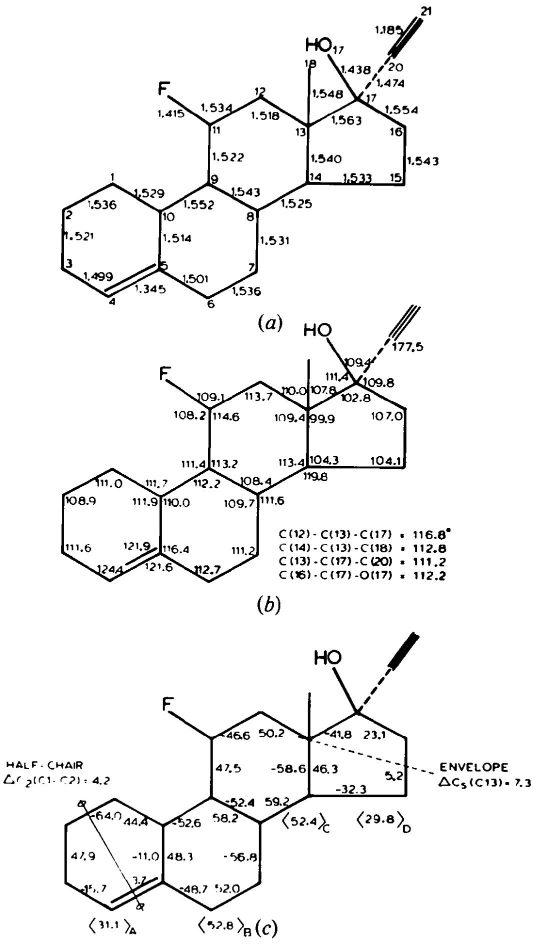

Fig. 2. Intramolecular dimensions of 11β-fluorolynestrenol. (*a*) Bond distances (Å); σ range = 0·002–0·004 Å. (*b*) Bond angles (°); σ range = 0·1–0·2°. (*c*) Endocyclic torsion angles (°). A torsion angle α–β–γ–δ is positive if, when viewed down the β–γ bond, the α–β bond will eclipse the γ–δ bond when rotated less than 180° in a clockwise direction. The numbers in brackets, ⟨ ⟩, are the average intra-ring dihedral angles.

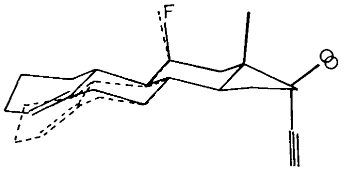

Fig. 3. Superposition of the *C* and *D* rings in the structure of the 11β-fluoro and 11β-methyl derivatives of lynestrenol.

between the axial 11β-fluoro substituent and the axial C(18) is 2·975 Å. This is only slightly longer than the 11β-hydrogen to C(18) distance of 2·84 Å in lynestrenol. This similarity in overall conformation of the 9α-fluorolynestrenol and lynestrenol is consistent with the similarity of their progestational activity when contrasted with the more active 11β-methyllynestrenol structure (Rohrer, Hazel, Duax & Zeelen, 1976) which has a bowed conformation (Fig. 3). The *D* ring has a C(13) β conformation.

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# 5,5′-Dithiobis(3-methyl-1,3,4-thiadiazoline-2-thione)

By Sine Larsen

*Chemical Laboratory* IV, *The H. C. Ørsted Institute, Universitetsparken* 5, *DK*-2100 *Copenhagen, Denmark*

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**Abstract.** $C_6H_6N_4S_6$, $M_r$ = 326·53, monoclinic, $C2/c$, $a$ = 20·08 (2), $b$ = 5·150 (5), $c$ = 12·17 (1) Å, $\beta$ = 97·60 (6)°, $D_x$ = 1·79, $D_c$ = 1·74 Mg m$^{-3}$, $Z$ = 4. The 1,3,4-thiadiazoline ring is planar and the bond lengths show that it has extensive conjugation.

**Introduction.** In the study of the reaction between thiophosgene and hydrazines (Anthoni, Dahl, Eggert, Larsen & Nielsen, 1976), which mainly produces trithiocarbonates, the title compound was obtained as a byproduct. The structure analysis was undertaken to prove that the postulated structure is correct and to obtain structural data for the 1,3,4-thiadiazoline ring.

The space group and preliminary cell parameters were determined from photographs. Systematic absences are *hkl*, $h + k$ odd; *h0l*, *l* odd; space group *C*2/*c* or *Cc*. A rhombic-shaped crystal, 0·04 mm thick, with the rhombic diagonals 0·15 and 0·36 mm was used for both cell refinement and data collection on a Picker FACS-1 diffractometer with graphite-monochromated Mo *K*α radiation ($\lambda$ = 0·71069 Å) at 295 K. By operation of the diffractometer in a $\theta$–$2\theta$ scan mode at a rate of 2° min$^{-1}$ in $2\theta$, intensities were recorded for the reflections in the hemisphere ($h \geq 0$) in the range $2{\cdot}4 \leq 2\theta \leq 52°$. The symmetry-related reflections were averaged to give 1190 independent reflections. 751 reflections with $I/\sigma(I) \geq 2{\cdot}0$ were used for the analysis.

Three standard reflections were measured after every 40 reflections and showed that no deterioration or misalignment had occurred. Lorentz and polarization but no absorption corrections were applied [$\mu$(Mo *K*α) = 1·031 mm$^{-1}$].

The structure was solved with *MULTAN* (Germain, Main & Woolfson, 1971). On the assumption that the molecule possesses a twofold axis and thus crystallizes in the space group *C*2/*c*, a standard run revealed the eight non-hydrogen atoms. The structure was refined by the least-squares method minimizing $\sum w||F_o| - |F_c||^2$. A difference synthesis calculated after anisotropic refinement showed the positions of the three H atoms which were given a fixed isotropic temperature factor, $U$ = 0·07 Å$^2$. The weights used in the final cycles (Nielsen, 1977) were given by $w^{-1} = 3{\cdot}11\sigma(F)^2 + 0{\cdot}052F - 0{\cdot}00012F^2$. Scattering factors were taken from Cromer & Mann (1968) for C, N and S and from Stewart, Davidson & Simpson (1965) for H. In the last cycle the maximum shift of parameters was 0·03$\sigma$. $R = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_w = (\sum w||F_o| - |F_c||^2/\sum w|F_o|^2)^{1/2}$ were 0·044 and 0·035 respectively for the 751 observed reflections. The goodness of fit $G = [\sum w||F_o| - |F_c||^2/(N - M)]^{1/2}$ = 0·80. The calculations were made with the XRAY system (1972). The final coordinates are shown in Table 1.*

Table 1. *Final positional parameters with e.s.d.'s in parentheses*

| | *x* | *y* | *z* |
|---|---|---|---|
| S(1) | 0·95087 (6) | 0·7053 (2) | 0·08437 (10) |
| C(2) | 0·8781 (2) | 0·8882 (9) | 0·0545 (4) |
| N(3) | 0·8357 (2) | 0·8166 (8) | 0·1255 (3) |
| N(4) | 0·8559 (2) | 0·6262 (8) | 0·2014 (3) |
| C(5) | 0·9146 (2) | 0·5518 (9) | 0·1881 (3) |
| S(2) | 0·86652 (7) | 1·1081 (3) | −0·04390 (11) |
| C(6) | 0·7722 (3) | 0·9401 (14) | 0·1350 (6) |
| S(3) | 0·95306 (7) | 0·3015 (2) | 0·27193 (10) |
| H(1) | 0·755 (3) | 1·021 (11) | 0·082 (4) |
| H(2) | 0·743 (3) | 0·822 (10) | 0·118 (4) |
| H(3) | 0·777 (3) | 1·051 (10) | 0·192 (4) |

Table 2. *Deviations* (Å) *of atoms from a least-squares plane*

Atoms marked with an asterisk were used to calculate the plane.

| | | | | | |
|---|---|---|---|---|---|
| S(1) | 0·004* | C(2) | −0·004* | N(3) | 0·003* |
| N(4) | 0·002* | C(5) | −0·004* | S(2) | −0·011 |
| C(6) | 0·128 | S(3) | −0·050 | | |

Table 3. *Bond distances* (Å) *and angles* (°) *involving the non-hydrogen atoms with e.s.d.'s in parentheses*

| | | | |
|---|---|---|---|
| S(1)–C(2) | 1·736 (5) | S(1)–C(5) | 1·731 (5) |
| C(2)–N(3) | 1·343 (6) | C(5)–N(4) | 1·269 (6) |
| C(2)–S(2) | 1·643 (5) | N(3)–N(4) | 1·371 (6) |
| N(3)–C(6) | 1·443 (8) | C(5)–S(3) | 1·758 (5) |
| C(6)–H(1) | 0·81 (5) | S(3)–S(3') | 2·026 (3) |
| C(6)–H(2) | 0·85 (5) | | |
| C(6)–H(3) | 0·90 (5) | | |
| S(1)–C(2)–N(3) | 107·7 (3) | C(5)–S(1)–C(2) | 88·7 (2) |
| S(1)–C(2)–S(2) | 124·1 (3) | S(1)–C(5)–N(4) | 116·3 (3) |
| S(2)–C(2)–N(3) | 128·2 (4) | S(1)–C(5)–S(3) | 124·3 (3) |
| C(2)–N(3)–N(4) | 118·3 (4) | S(3)–C(5)–N(4) | 119·5 (4) |
| C(2)–N(3)–C(6) | 124·9 (5) | N(3)–N(4)–C(5) | 109·1 (4) |
| N(4)–N(3)–C(6) | 116·6 (4) | C(5)–S(3)–S(3') | 101·5 (2) |

**Discussion.** The atom numbering is illustrated on Fig. 1, which shows the molecule seen perpendicular to the twofold axis. Table 2 shows that the 1,3,4-thiadiazoline ring is planar and that the substituents are only slightly displaced from the plane. Table 3 lists the bond lengths and angles which show that conjugation in the ring is just as pronounced as in the analogous unsaturated ring. 1,3,4-Thiadiazole has been studied by microwave

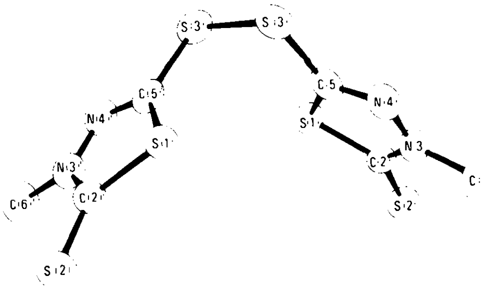

Fig. 1. 5,5'-Dithiobis(3-methyl-1,3,4-thiadiazoline-2-thione) seen perpendicular to the twofold axis.

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33910 (5 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

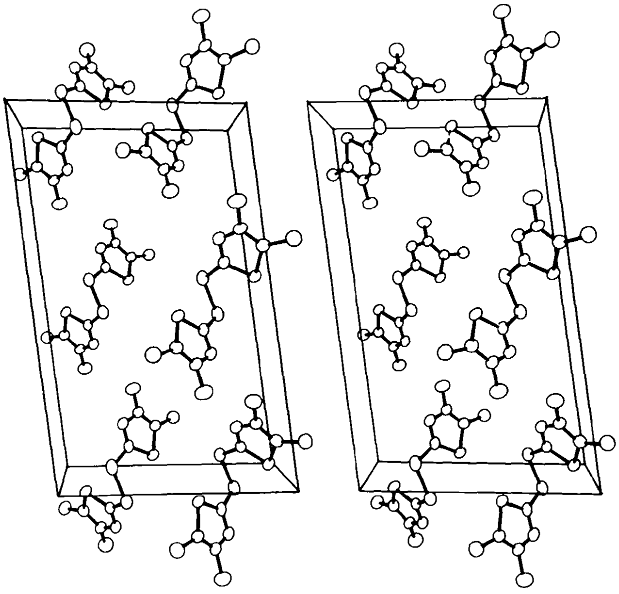

Fig. 2. Stereoscopic drawing of the packing viewed along *b*.

spectroscopy (Bak, Nygaard, Pedersen & Rastrup-Andersen, 1966), electron diffraction (Markov & Stølevik, 1970) and X-ray diffraction (la Cour, 1974). It is remarkable that the C(2)—S(1)—C(5) moiety in this structure seems unchanged from the similar part in 1,3,4-thiadiazole, and that the N—N bond in the partly saturated 1,3,4-thiadiazoline ring is of the same length as in the unsaturated 1,3,4-thiadiazole ring.

The N(4)—C(5) distance corresponds closely to a C—N double bond and the dimensions involving the unsaturated N atom are similar to those in 2,4-dimethyl-1,2,4-thiadiazolidine-3,5-thione (Raston, White, Willis & Varghese, 1974). The S—S length of 2·026 Å is identical to that in diphenyl disulphide (Lee & Bryant, 1969).

The molecular packing is illustrated in Fig. 2. Except for the distance between N(4) and S(2) of 3·37 Å all the interatomic distances are greater than the sum of the van der Waals radii (Bondi, 1964).

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# 3,7-Anhydro-6,8-*O*-benzyliden-4-desoxy-D-*talo*-oct-2-ulosonsäureethylester-2-ethylendithioacetal

VON ELISABETH ROSSMANITH UND K. H. KLASKA

*Mineralogisch-Petrographisches Institut der Universität Hamburg, D-2 Hamburg* 13, *Grindelallee* 48, *Bundesrepublik Deutschland*

UND H. BÜNSCH UND H. PAULSEN

*Institut für Organische Chemie und Biochemie der Universität Hamburg, D-2 Hamburg* 13, *Martin-Luther-King-Platz* 6, *Bundesrepublik Deutschland*

(*Eingegangen am* 9. *Januar* 1978; *angenommen am* 9. *August* 1978)

**Abstract.** Ethyl 3,7-anhydro-6,8-*O*-benzylidene-4-deoxy-2-ethylenedithio-D-*talo*-2-octulosonate (ADO), $C_{19}H_{24}O_6S_2$, $M_r = 412·5$, orthorhombic, space group $P2_12_12_1$, $a = 6·524$ (1), $b = 7·466$ (1), $c = 41·391$ (5) Å, $Z = 4$, $D_x = 1·359$ g cm$^{-3}$, $\mu$(Cu $K\alpha$) = 26·0 cm$^{-1}$, $V = 2016·1$ Å$^3$; $F(000) = 872$. The structure was